Letters to the Editor

The Board of Editors does not hold itself responsible for opinions expressed in the letters published in this section. The notes containing short reports of original investigations communicated to this section should not contain many figures and should not exceed 500 words in length. The contributions reaching the Secretary by the 15th of any month may be expected to appear in the issue for the next month. No proof will be sent to the author.

16

VARIATION OF THE RELAXATION TIME AND THE MOLAR FREE ENERGY OF ACTIVATION WITH THE C-AXIS SPACING (d_{001})OF SOME COMPLEXES OF BENTONITE

SABITA GHOSH

KHAIRA LABORATORY OF PHYSICS,

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

(*Received May* 10, 1965)

Plate—II

The clay mineral montmorillonite (commonly called bentonite) displays an expansion in c-axis spacing depending on size and the charge of the exchangeable cations (Barshad, 1950) and the adsorbed water molecules (Grim, 1953) between the negatively charged silicate layers. The extent of expansion depends on the interaction between the binding force, which acts from layer to layer through the interlayer cations, and the expansion force created by the adsorption of the water molecules on the interlayer surfaces (Jonas, *et al* 1960).

In the present note, it is reported how the dielectric properties vary with the c-axis expansion in different complexes of bentonite brought about by the cation exchange process. To observe the variation in the c-axis spacing (d_{001}) the powdered raw sample (England) was sieved through a 200-mesh screen and brought in suspension in water. The complexes of the mineral with H^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+}-ions were made by percolating the suspension through different columns of the cation exchange resin (IR 120, Amberlite) previously converted into the desirable cation forms. All the samples were dried under same relative humidity and the X-ray photographs were taken with CuK_α radiation (using Ni-filter) in a Debye-Scherrer camera of radius 9.956 cm. One such photograph is shown in Fig. 1.

Fig. 1.—X-ray Photograph for Mg. Complex

The loss-tangent (tan δ) and the dielectric constant (ϵ') of the above clay-complexes were measured at 30°C with the help of a Q-meter within the range of frequencies from 100 Kc/sec to 4 Mc/sec following the same method as adopted previously by the author (Ghosh, 1962). The relaxation times (τ) for these samples were then determined from the frequency of maximum absorption and hence the values of molar free energy of activation for dipole relaxation were calculated from the formula, $\frac{1}{\tau} = \frac{kT}{h} \exp \frac{-\Delta G^*}{RT}$ where ΔG^* is the molar free energy of activation and the other symbols have their usual significance. The values of relaxation time for *H*, *Li*, Na, K, Mg, Ca and Ba-complexes are 6.10×10^{-7} sec., 7.53×10^{-7} sec., 1.03×10^{-6} sec., 1.05×10^{-6} sec., 4.81×10^{-7} sec., 6.10×10^{-7} sec. and 7.53×10^{-7} sec. respectively.

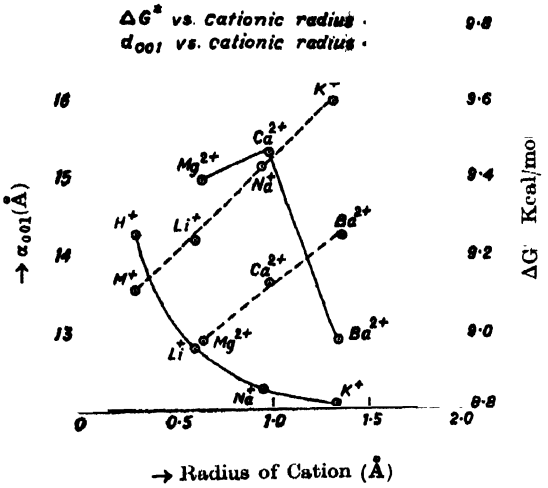

Fig. 2. Variation of d_{001} and ΔG^* with cationic radius.

The observed variations of the *c*-axis spacing (d_{001}) and activation energy (ΔG^*) with the radius of the cations is shown in Fig. 2 for monovalent and divalent cation complexes and can be understood in the following manner : Since the molar free energy of activation is found to increase with the cationic radii, it can be said that the binding with the two silicate layers is stronger for the larger cations and for more polarizable ones in these cases. This is consistent with the observation that there is a gradual decrease in *c*-axis spacing with the cationic radii in the case of monovalent and divalent cations except for Ca^{2+}-ion. This decrease of spacing indicates that the binding force, acting through the charged material between the silicate layers, gradually increases with the radius of the cations. In case of Ca-complex (having larger spacing than Mg-complex) the increase in activation energy may be due to the fact that Ca^{2+} is more polarizable than Mg^{2+} which increases the activation energy.

A significant feature is to be noted from Fig. 2. Considering the valencies of the cations having nearly the same size, viz., (Mg^{2+}, Li^{+}), (Ca^{2+}, Na^{+}), (Ba^{2+}, K^{+}) etc., it can be seen that the activation energy for the divalent cation is less than that for monovalent cation for each of the Sepairs. This indicates lowering of binding between the silicate layers in case of divalent cations. This lowering of binding energy is evidently due to the increase of spacing by the greater adsorption of water molecules between the silicate layers for divalent cation-complex.

My sincere thanks are due to Professor S. R. Khastgir, under whose guidance the present work was carried out.

REFERENCES

Barshad, I., 1950, *Am. Min.*, **35**, 225.
Ghosh, S., 1962, *J. Chem. Phys.*, **37**, 199.
Grim, R. E., Clay Mineralogy, (McGraw-Hill Book Company, Inc., 1953), pp. 257-260.
Jonas, E. and Roberson Herman E., 1960, *Am. Min.*, **45**, 828.